

REMARKS

Undersigned Applicants' representative wishes to thank Examiner Ferguson for the helpful and courteous discussion regarding the merits of this application held on August 25, 2006. The substance of this discussion will be expanded upon in the remarks made below. The suggestions made by Examiner Ferguson in both the interview and the Office Action have been adopted, therefore obviating the indicated rejections.

The present invention is directed to a nanolayered composite polymer structure that possesses a dynamically variable refractive index. The critical considerations are that 1) component polymers with substantially different elastic moduli are arranged in a layered structure; 2) the layer thickness of each layer is sufficiently thin so that the composite behaves as an effective medium, in other words, a single unique value of a property, a single refractive index; and 3) the component polymers have substantially different refractive indices. Such a composite possesses a transparency comparable to the component polymers. (It is not a dielectric mirror reflector). This is in clear contrast to the common understanding at the time the application was filed. At that time the understanding was that multilayer composites with a large number of layers of alternating polymers with different refractive indices have mirror-like properties. Thus, the prior art reference of Kollaja et al., cited by the Examiner, states:

Multilayer films have also been described. For example, constructions having up to several thousand layers of alternating polymers with different refractive indices have been shown to have mirror-like properties. (U.S. Patent 6,579,601, column 1, lines 36-39)

The forces that induce the refractive index changes can be applied mechanically or electrically by electrodes attached to the nanolayered composite polymer structure. This provides a novel mechanism for an electro-optical response.

As disclosed in the present application:

The fabrication of elastomeric multilayer structures with layer spacings much less than the wavelength of visible or near infrared (NIR) light has never been reported. It has not been recognized that such a composite will behave as a dynamically variable refractive index. (paragraph [0006] of the present application as filed.

Applicants submit that based on the above statement of Kollaja et al. and the above disclosure in the present application, the present invention is contrary to the understanding of the prior art at the time of the invention. Applicants respectfully wish to bring to the Examiner's attention the following court decision:

“...because the insight was contrary to the understanding and expectations of the art, the structure effectuating it would not have been obvious to those skilled in the art” *Schenck v. Norton Corp.*, 218 USPQ 698 (Fed. Cir. 1983).

Response to the Restriction Requirement

The Office has restricted this application under 35 U.S.C. §121 as follows:

- I. Claims 1-18, drawn to a multilayer structure.
- II. Claim 19, drawn to method of manufacturing.

Applicants have elected, with traverse, Group I, Claims 1-18.

Restriction is only proper if the restricted inventions are independent or patentably distinct and there is a serious burden placed on the Examiner if restriction is not required (MPEP 803). The burden is on the Examiner to provide reasons and/or examples to support any conclusion of patentable distinctness between the restricted invention (MPEP 803).

Applicants respectfully traverse the restriction requirement on the grounds that no adequate reasons and/or examples have been provided to support conclusions of patentable distinctness between the restricted invention and that a serious burden is placed on the Examiner if restriction is not required.

Further, the attention of the Examiner is respectfully directed to the following concerning linking of claims:

“However, if applicant elects claims directed to the product, and a product claim is subsequently found allowable, withdrawn process claims which depend from or otherwise include all the limitations of the allowable product claims will be rejoined”(MPEP 821.04)

Further,

The linking claims must be examined with the invention elected, and should any linking claim be allowed, the restriction requirement must be

withdrawn. Any claim(s) directed to the nonelected invention(s), previously withdrawn from consideration, which depends from or includes all the limitations of allowable linking claims must be rejoined and will be fully examined for patentability. Where such withdrawn claims have been canceled by applicant pursuant to restriction requirement, upon the allowance of the linking claim(s), the examiner must notify applicant that any canceled, nonelected claim(s) which depends from or include all the limitations of the allowable linking claim may be reinstated by submitting the claim(s) in an amendment. Upon entry of the amendment, the amended claim(s) will be fully examined for patentability. (MPEP 809)

Response to Claim Objections

Claim 2 has been canceled thus obviating the objection to that claim.

Claim 13 was amended in accordance with the Examiner's suggestion, thus obviating the objection.

Applicants respectfully request the withdrawal of the objections.

The rejection of Claims 1-2, 6-7 and 11-12 under 35 U.S.C. 102(b) as being anticipated by U.S. Patent 5,912,069 to Yializis et al. is respectfully traversed.

Yializis et al. is directed to a "metallpolymer" laminate produced by sequential deposition of the metal and polymer layers. The above cited prior art reference states:

"...the metallpolymer laminateis produced in a vacuum environment by successive, sequential deposition of the metal and polymer layers in an ultra high speed vacuum nanotechnology process that forms metal layers separated by radiation cross-linked multifunctional acrylate polymer materials.

Further, metal-polymer nanolaminate products, e.g., powders, are fabricated from bulk nanolaminate material, composed of thousands of **alternating metal and polymer layers**. (column 1, line 65 to column 2, line 9, bold emphasis added)

In contrast, the present claims require a structure exhibiting a single unique refractive index that can be varied. Hawley's *Condensed Chemical Dictionary* defines "refraction" as follows:

“refraction. The change in direction (apparent bending) of a light ray passing from one medium to another of different density, as from air to water or glass. The ratio of the sine of the angle of incidence to the sine of the angle of the refraction is the index of refraction of the second medium. Index of refraction of a substance may also be expressed as the ratio of the velocity of light in a vacuum to its velocity in the substance. It varies with the wavelength of the incident light, temperature, and pressure. Given the usual light source is the D line of sodium, the standard temperature being 20C, the expression of refractive index is 20/D” (Hawley’s *Condensed Chemical Dictionary*, Twelfth Edition, Van Nostrand Reinhold Company, New York, 1993, page 997 third entrances, pertinent pages attached herewith for convenience).

Clearly, the nanolaminate of the above cited prior art reference, comprised of alternating metal and polymer layers cannot exhibit a measurable refractive index, since any light passing through the polymer layer will be reflected by the metal layer.

Accordingly, Yializis et al. neither discloses nor suggests the present invention.

Applicants respectfully request the withdrawal of the rejection.

The rejection of Claims 1-4, and 10-12 under 35 U.S.C. 102(b) as being anticipated by U.S. Patent 5,278,694 to Wheatley et al. is respectfully traversed.

What distinguishes the present invention from the cited prior art of Wheatley et al. is that Wheatley et al. is directed to a “multilayered polymeric reflective body” (column 2, line 41) while the present invention is directed to multilayered structure of transparent layers exhibiting a refractive index. Thus Wheatley et al. specifically state:

The terms "reflective", "reflectivity", "reflection", and "reflectance" as used herein refer to total reflectance (i.e., ratio of reflected wave energy to incident wave energy) sufficiently specular in nature **such that the polymeric body has a metallic appearance.** (Column 2, lines 44-49, bold emphasis added).

Accordingly, Wheatley et al. teaches away from the present claims which require transparent layers forming a structure exhibiting a single refractive index that can be varied. The definition of refraction and refractive index was stated above as per Hawley’s *Condensed Chemical Dictionary* defines

The absence of internal reflectivity is achieved in the present invention by the layer thickness being less than one quarter of the wavelength of interest (as disclosed on page 4, paragraph [0020] in the present application)

Clearly, Wheatley et al. neither discloses nor suggests the present invention. In contrast Wheatley et al. teaches away from the present claims. Applicants respectfully request the withdrawal of the rejection.

The rejection of Claims 1-6 and 8-18 under 35 U.S.C. 102(e) as being anticipated by U.S. Patent 6,579,601 to Kollaja et al. is respectfully traversed.

Kollaja et al. is directed to conformable multilayer films for use in graphics applications, where stress relaxation and strain recovery are important and in auto paint masking tapes, where in addition, minimal ghosting is also desired (column 1, lines 53-58). However, Kollaja et al. has not recognized the importance of the polymeric materials being transparent, or the layer thickness being less than one quarter of the wavelength of interest or that the refractive index of the structure can be varied by tensile, compressive or shear force all of which are limitations of the present claims. The MPEP under "ONLY RESULT-EFFECTIVE VARIABLES CAN BE OPTIMIZED", states:

A particular parameter must first be recognized as a result-effective variable, i.e., a variable which achieves a recognized result, before the determination of the optimum or workable ranges of said variable might be characterized as routine experimentation." (MPEP 2144.05; *In re Antonie*, 559 F.2d 618, 195 USPQ 6 (CCPA 1977).

The fact that Kollaja et al. has not recognized the importance of the polymeric materials being transparent, subject matter claimed in the present claims, is clear from the fact that almost all the examples of Kollaja et al. contain a layer consisting of a blend. Polymer blends are not transparent unless they are miscible. The treatise *Polymer-Polymer Miscibility* (Academic Press, New York, 1979) states:

"The vast majority of polymer pairs form two-phase blends after mixing as can be surmised from the small entropy of mixing for very large molecules. These blends are generally characterized by **opacity**, distinct thermal transitions, and poor mechanical properties. However, special precautions in the preparation of two-phase blends can yield composites

with *superior* mechanical properties.” (Page 7, paragraph 5, bold emphasis added, pertinent pages submitted herewith).

The same treatise states:

“But experience has shown that immiscibility in polymer blends is rarely well concealed, revealing itself as **opacity**, delamination, double glass transition, or combinations of these properties.” (Page 4, lines 11-13, bold emphasis added, pertinent pages submitted herewith).

It is further, well known to those skilled in the art, that in order for a blend to exhibit good mechanical properties the components of the two-component system should not form a homogeneous phase (miscible), and thus, useful blends are not homogeneous (transparent). The treatise *Polymer Blends and Composites* (Plenum Press, New York, 1976) states:

“It should be pointed out that in order to develop superior mechanical properties in a two-component polymer system, the components should not be so incompatible that they do not wet, **nor so mutually soluble that they form one homogeneous phase** (Tobolsky, 1960, pp. 81-82). Most of the presently important systems are compatible to the extent that a slight (but usually unknown!) degree of mixing takes place, or interfacial bonding is developed directly, as in grafts or blocks.” (Page 59, first paragraph, bold emphasis added, pertinent pages are submitted herewith).

Thus, Kollaja et al. in Examples 1-10 uses as flexible layers a blend of two polymer, RexflexTM and BynelTM (column 15, lines 62-63); in Examples 11-13 uses a mixture of RexflexTM with Filler A (column 18, lines 13-14); in Examples 14-15 uses the same polymers as in Example 1.

Clearly, Kollaja et al. has not recognized the importance of the transparent polymeric materials and his multilayer films cannot exhibit refractive index or that the refractive index can be varied by tensile, compressive or shear force.

Further, as indicated in Silverstri vs Grant, 496 F.2d 593,181 USPQ 706 (CCPA 1974), it is a principle of patent law that an accidental and unappreciated duplication of an invention does not defeat the patent right of one who, though late in time, was the first to recognize that which constitutes the invention subject matter. See also In re Marshall, 578 2nd 301 198 USPQ 344 (CCPA 1978).

Clearly, Kollaja et al. neither discloses nor suggests the present claims.
Applicants respectfully request the withdrawal of the rejection.

The rejection of Claim 7 under 35 U.S.C. 103(a) as being unpatentable over U.S. Patent to Kollaja et al. is respectfully traversed.

Applicants submit that Claim 7 is patentable by virtue of its dependence on Claim 1, which Applicants consider patentable in view of the present amendment to that claim. Applicants respectfully request the withdrawal of the rejection.

The rejection of Claims 1-4, 6, 8, 10-11 and 13-15 under 35 U.S.C. 102(b) as being anticipated by U.S. Patent 6,045,895 to Hyde et al. is respectfully traversed.

Hyde et al. is directed to multilayer films having pressure sensitive adhesive layers. What distinguishes Hyde et al. from the present claims is that Hyde et al. has not recognized the importance of the polymeric materials forming the layers being transparent or that the refractive index of the multilayered structure can be varied by tensile, compressive or shear force, subject matter claimed in the present application. In contrast, Hyde et al. discloses "blends" (column 2, lines 22-27 and column 8, lines 7-22). As pointed out above (in the response to the rejection over Kollaja et al), blends are opaque polymers, not transparent and the structure cannot exhibit a refractive index, as defined above (in Hawley's Dictionary). Further, Hyde et al. in practically all his Examples uses block copolymers, such as Kraton. The *Handbook of Thermoplastic Elastomers* (herein after *Handbook*) (Van Nostrand Reinhold Company, New York, 1979) describes block copolymers, such as Kraton, as consisting of two or more segments of different composition. The *Handbook* states:

"Block polymers are usually considered to consist of two or more segments of different composition joined end to end" (page 72, second paragraph to page 74 end of first paragraph, pertinent pages submitted herewith).

Figure 3-2 in the above *Handbook* (page 74, pertinent page submitted herewith for convenience) clearly shows the heterogeneous structure of a block polymer as explained on page 73 second and third paragraphs of the *Handbook*.

Clearly, Hyde et al. cannot inherently exhibit the transparency or the refractive index requirements of the present claims. Applicants respectfully request the withdrawal of the rejection.

The rejection of Claims 1-2 under 35 U.S.C. 102(b) as being anticipated by Applicant's own admission is respectfully traversed.

As pointed out above, the critical characteristics of the present invention are that 1) component polymers with substantially different elastic moduli are arranged in a layered structure; 2) the layer thickness of each layer is sufficiently thin so that the composite behaves as an effective medium; and 3) the component polymers have substantially different refractive indices, subject matter claimed in Claim 1 of the present application.. Such a composite possesses a transparency comparable to the component polymers.

Applicants have neither disclosed nor suggested that the above limitations are known in the prior art. As a matter of fact, Applicants submit that to their knowledge the fabrication of elastomeric multilayer structures with layer spacings much less than the wavelength of visible or near infrared (NIR) light, so that the composite behaves as a dynamically variable effective medium has never been reported. As pointed out above the present invention was contrary to the understanding of those skilled in the art at the time of the invention.

Applicants respectfully request the withdrawal of the rejection.

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Amdt. Dated 08/26/2006
Reply to Office action of 05/03/2006

Applicants submit that the application is now ready for allowance and early notification to that effect will be greatly appreciated.

Customer No.: 28727

Respectfully submitted,

A handwritten signature in black ink, appearing to read 'Stamatios Mylonakis', written in a cursive style.

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MARKED-UP SHEET

1. A multilayer polymer structure comprising,
a plurality of at least two alternating layers A and B represented by formula
(AB)_x, where $x = 2^n$, and n is in the range of from 4 to 15;
wherein layer A is comprised of component (a) and layer B is comprised of
component (b); ~~and~~
said alternating layers are comprised of different polymers exhibiting differences
in the index of refraction and in the elastic moduli;
wherein the layer thickness of said layer A and B are less than one quarter of the
wavelength of interest;
wherein said multilayer polymer structure behaves as an effective medium and
wherein said structure exhibits a single refractive index;
wherein said effective medium polymeric materials are transparent; and
wherein the refractive index of said ~~component (a) or component (b)~~ multilayered
structure effective medium material can be varied by tensile, compressive or shear force.

5. The multilayer structure of Claim 1, comprising a plurality of at least
three alternating layers A, B and C, represented by formula (ABC)_x, wherein layer A is
comprised of component (a), layer B is comprised of component (b) and layer C is
comprised of component (c); and wherein said components (a), (b) and (c) may be the
same or different provided that the refractive index of at least one of components (a), (b)
or (c) can be varied by tensile, compressive or shear force; and wherein the thickness of

each layer is less than one quarter of the wavelength at which the refractive index of the material is measured.

7. The multilayer structure of Claim 1, wherein the thickness of each layer is in the order of from 5 nanometers and 650 nanometers; provided that the thickness of each layer is less than one quarter of the wavelength at which the refractive index of the material is measured or the material is used.

13. The multilayer structure of ~~Claim 2~~ Claim 3, wherein said glassy material is selected from the group consisting of a polyethylene naphthalate, a polyethylene naphthalate isomer, a polyalkylene terephthalate, a polyetherimide, a styrenic polymer, a polycarbonate, a poly(meth)acrylate, a cellulose derivative, a polyalkylene polymer, a fluorinated polymer, a chlorinated polymer, polyvinylacetate, a polyether-amide, a styrene-acrylonitrile copolymer, styrene-ethylene copolymer, poly(ethylene-1,4-cyclohexylenedimethylene terephthalate) and blends thereof.

14. The multilayer structure of ~~Claim 12~~ Claim 13, wherein said polyethylene naphthalate isomer is selected from the group consisting of 2,6-, 1,4-, 1,5-, 2,7-, and 2,3- polyethylene naphthalate; the polyalkylene terephthalate is selected from the group consisting of polyethylene terephthalate, polybutylene terephthalate, and poly-1,4-cyclohexanedimethylene terephthalate; the polyimide is a polyacrylic imide; the styrenic polymer is selected from the group consisting of atactic polystyrene, isotactic polystyrene, syndiotactic polystyrene, α -methyl-polystyrene, and para-methyl-polystyrene; the polycarbonate is bisphenol-A-polycarbonate (PC); the poly(meth)acrylate is selected from the group consisting of poly(isobutyl methacrylate),

poly(propyl methacrylate), poly(ethyl methacrylate), poly(methyl methacrylate), poly(butyl acrylate) and poly(methyl acrylate); the cellulose derivative is selected from the group consisting of ethyl cellulose, cellulose acetate, cellulose propionate, cellulose acetate butyrate and cellulose nitrate; the polyalkylene polymer is selected from the group consisting of polyethylene, polypropylene, polybutylene, polyisobutylene and poly(4-methyl)pentene; the fluorinated polymer is selected from the group consisting of perfluoroalkoxy resins, polytetrafluoroethylene, a fluorinated ethylene-propylene copolymer, polyvinylidene fluoride and polychlorotrifluoroethylene; the chlorinated polymer is selected from the group consisting of polydichlorostyrene, polyvinylidene chloride and polyvinylchloride.

15. The multilayer structure of ~~Claim 2~~ Claim 3, wherein said elastomeric polymer is selected from the group consisting of poly(ethylene-octene), acrylic rubber, brominated isobutylene-isoprene, butadiene rubber, butadiene-styrene-vinyl pyridine, butyl rubber, chlorinated isobutylene-isoprene, a chlorinated polyethylene, chloroprene, chlorosulfonated polyethylene, epichlorohydrin rubber, a homopolymer with ethylene oxide, a copolymer with ethylene oxide, ethylene-propylene-diene, ethylene-propylene rubber, a fluorocarbon rubber, natural rubber, nitrile rubber, polyisoprene, polysulfide rubber, silicone rubber, styrene-butadiene, urethane rubber, blends and formulated rubbers thereof.

16. The multilayer structure of ~~Claim 8~~ Claim 9, wherein said barrier is selected from the group consisting of hydrolyzed ethylene vinyl acetate, a copolymer of polyvinylidene chloride, a nitrile polymer, and nylons.

17. The multilayer structure of ~~Claim 8~~ Claim 9, wherein said barrier layer is bonded using an adhesive material.

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18. The multilayer structure of ~~Claim 16~~ Claim 17, wherein said adhesive material is a maleic anhydride grafted polyolefin.

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Hawley's

Condensed Chemical

Dictionary

TWELFTH EDITION

Revised by

Richard J. Lewis, Sr.



VAN NOSTRAND REINHOLD COMPANY

New York

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reforming. Decomposition (cracking) of hydrocarbon gases or low-octane petroleum fractions by heat and pressure, either without a catalyst (thermoforming) or with a specific catalyst (molybdena, platinum). The latter method is the more efficient and is used almost exclusively in the U.S. The chief cracking reactions are (1) dehydrogenation of cyclohexanes to aromatic hydrocarbons; (2) dehydrocyclization of certain paraffins to aromatics; (3) isomerization, i.e., conversion of straight-chain to branched-chain structures, as octane to isooctane. These result in substantial increase in octane number. Steam reforming of natural gas is an important method of producing hydrogen by the reaction $\text{CH}_4 + \text{H}_2\text{O} \rightarrow 3\text{H}_2 + \text{CO}$; steam reforming of naphtha is used to produce synthetic natural gas. See also hydroforming; "Platforming."

"Refractaloy" [Westinghouse]. TM for a nickel-cobalt-chromium-molybdenum-iron alloy. Type 26 is a precipitation-hardenable material using titanium as the hardening agent, and having high strength, high ductility, and corrosion resistance up to 1450F. Use: Gas turbine discs, bolting, and blading are typical applications.

refraction. The change in direction (apparent bending) of a light ray passing from one medium to another of different density, as from air to water or glass. The ratio of the sine of the angle of incidence to the sine of the angle of refraction is the index of refraction of the second medium. Index of refraction of a substance may also be expressed as the ratio of the velocity of light in a vacuum to its velocity in the substance. It varies with the wavelength of the incident light, temperature, and pressure. Given the usual light source is the D line of sodium, the standard temperature being 20C, the expression of refractive index is $20/D$.

refractive. Descriptive of a substance having a high refractive index.

refractive index. See refraction.

refractometer. A device for determining the index of refraction of a material.

refractory. (1) An earthy, ceramic material of low thermal conductivity that is capable of withstanding extremely high temperature (1650–2200C) without essential change. There are three broad groups of these: (a) acidic (silica, fire-clay), (b) basic (magnesite, dolomite), and (c) amphoteric (alumina, carbon and silicon carbide). Their primary use is for lining steel furnaces, coke ovens, glass lehrs, and other continuous high-temperature applications. They are

normally cast in the form of brick and are sometimes bonded to assure stability. The outstanding property of these materials is their ability to act as insulators. The most important are fire-clay (aluminum silicates), silica, high alumina (70–80% Al_2O_3), mullite (clay-sand), magnesite (chiefly MgO), dolomite (CaO-MgO), forsterite (MgO-sand), carbon, chrome-ore magnesite, zirconia, and silicon carbide. See also specific entries.

(2) Characterizing the ability to withstand extremely high temperature, e.g., tungsten and tantalum are refractory metals, clay is a refractory earth, ceramics are refractory mixtures.

refractory ceramic fibers. (RCF's).

Properties: Man-made insulating fibers.

Use: To replace asbestos in coke ovens and industrial furnaces.

"Refrasil" [Carborundum]. TM for a group of materials having outstanding high-temperature resistance. Composed of white, vitreous fibers having up to 99% silicon dioxide content.

Available forms: Bulk fiber, batt, cloth, tape, sleeving, yarn, cordage, and flakes.

Use: Aircraft and missile ablative composites, industrial insulation and filtration applications, protective welding shield for spark and slag containment.

"Refrax" [Carborundum]. TM for silicon nitride-bonded silicon carbide refractories. Available in brick and precision-formed shapes and parts.

Use: Brazing and furnace fixtures; pumps and pump parts handling corrosives, abrasive slurries; rocket motor components; spray nozzles; burners; pyrometer protection tubes; sinker assemblies in wire aluminizing; bolts and nuts; valve parts; aluminum melting furnace linings and parts; conveyor parts.

refrigerant. Any substance that, by undergoing a change of phase (solid to liquid or liquid to vapor), lowers the temperature of its environment because of its latent heat. Melting ice, with a latent heat of 80 calories per gram, removes heat and exerts a considerable cooling effect. Most commercial refrigerants are liquids whose latent heat of vaporization results in cooling. Ammonia, sulfur dioxide, and ethyl or methyl chloride were once widely used. The flammability and toxicity of these compounds led to a search for safer refrigerants that resulted in the discovery of halogenated hydrocarbons, especially fluorocarbons, which are non-flammable. Under various trademarks, these are now generally used for domestic refrigeration and air-conditioning. Ice and circulating brine are still used for preservation of fish at sea and ammonia sys-

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Handbook of Thermoplastic Elastomers

Edited by

Benjamin M. Walker

President, Walker Engineering Associates



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3

Block Polymers

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3.1 INTRODUCTION

Discovery and development of new polymerization initiators in recent years have led to increased versatility in the preparation of elastomers. Polymer chemists now exert considerable control over microstructure, molecular weight features, branching, and combination of comonomers. This knowledge has been applied to a number of monomers including styrene, butadiene, and isoprene. Developments worthy of note are selectively structured polyisoprenes and polybutadienes and new random copolymers containing styrene; however, some of the most interesting of the many possible variations are block polymers. Butadiene-styrene polymers with two blocks have been produced since the early 1960s—these are useful in blends to modify properties and are used for this purpose in plastics and in vulcanized rubber compounds.¹ Copolymers with multiple blocks of polystyrene connected by rubbery segments form another group, which exhibits high strength and elastomeric characteristics without chemical cross-linking. The latter group is the subject of this chapter.

3.2 STRUCTURE AND COMPOSITION

3.2.1 Structure

Block polymers are usually considered to consist of two or more segments of different composition joined end to end. As segments can be various homopolymers

or copolymers, a very large number of block polymers can be prepared. However, this chapter will be primarily concerned with polymers prepared from styrene, butadiene, and isoprene. Even with this limitation, many combinations are possible. For example, segments could be polybutadiene, polystyrene, polyisoprene, or copolymers. Segments might be different isomers of a homopolymer, or segments may be arranged in various sequences. There could be two, three, or multiple blocks. Segments could be all-elastomeric or all-plastic. As this *Handbook* deals with thermoplastic rubbers, polymers that combine hard plastic-like segments with softer elastomeric segments are of particular interest. Such combinations, as exemplified by polystyrene and polybutadiene, form two separate phases and exhibit two glass-transition temperatures corresponding to each component.^{2,3} The polystyrene segments tend to associate but are restricted because of attachment to the flexible polybutadiene segments, and a network is formed. The polystyrene aggregates or domains serve as both cross-linking regions and as reinforcing particles. To form an effective network, there must be two or more hard segments in each molecule. These can be situated (see Figure 3-1) at the ends of a linear rubbery central block (a), or at the ends of a branched rubber molecule (c), or a number of them can be interspersed with rubbery blocks in a linear chain (b).

Polymers produced by Phillips Petroleum Co. and marketed under the trademark Solprene are described as radial (branched) "teleblocks" and are called *plastomers*. Polymers marketed by Shell Chemical Company under the trademark Kraton are reportedly linear.

The polystyrene domains in these block polymers can be spherical in shape (as shown in Figure 3-2), rodlike, or lamellar. Rods and lamellae break up when the polymer is stretched, and the structure then approaches that of Figure 3-2.

When these polymers are heated, the polystyrene domains soften, and the polymer will flow under pressure and thus can be molded, extruded, or otherwise

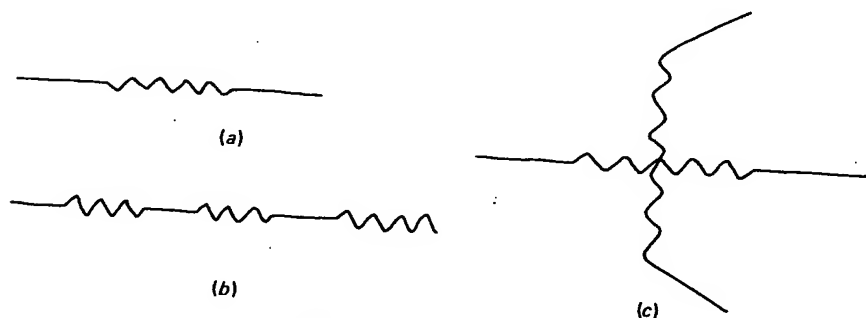


Figure 3-1. Polymer types.

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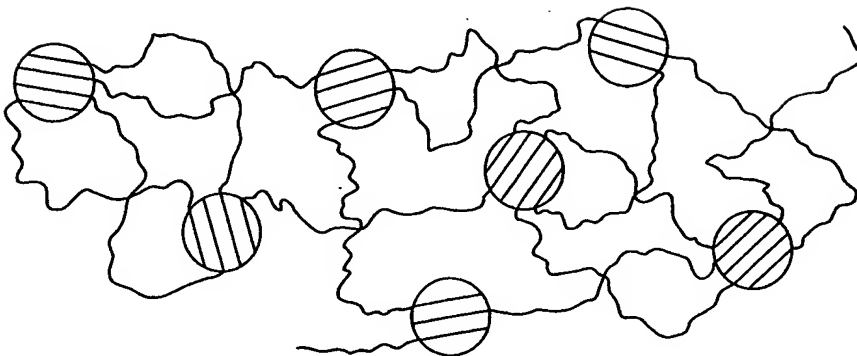


Figure 3-2. Polymer structure.

formed much like conventional thermoplastics. Upon cooling, the polystyrene segments reform into hard domains, and high strength is restored. Both polybutadiene and polyisoprene are useful as the elastomeric segment and in many respects provide similar behavior. Utilization of polyisoprene yields a softer material that shows reduced viscosity relative to polybutadiene.⁴

There are also polymers that have polystyrene end blocks and saturated elastomeric segments. These are newer versions and are more resistant to degradative effects caused by oxidation and by exposure to ultraviolet light or ozone.

3.2.2 Monomer Ratio

The monomer ratio in thermoplastic rubbers based on styrene and dienes is an important consideration and exerts a significant effect on properties. Increasing the amount of styrene will increase modulus and hardness.^{4,5} Hardness (Shore A) can be varied readily from approximately 40 to 90 or higher by increasing styrene as shown in Figure 3-3. Tensile strength (also shown in Figure 3-3) increases as more styrene is used, especially in the range of 5 to 20 percent styrene, although the trend is diminished at higher levels. The tensile values as shown may vary over a range depending on molecular weight, the structure of the polymer, and the methods used in molding and testing. Cold draw upon extension is often observed in polymers with more than 30 to 35 percent polystyrene.

Viscosities of the neat polymers⁶ or in adhesive formulations⁷ may rise as the styrene level is raised, although a maximum is reached in the first case. The morphology of the two-phase system can be dramatically altered (inversion of continuous phase) by large changes in the styrene content.⁸

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POLYMER BLENDS AND COMPOSITES

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2.5. THE INCOMPATIBILITY PROBLEM

It should be pointed out that in order to develop superior mechanical properties in a two-component polymer system, the components should not be so incompatible that they do not wet, nor so mutually soluble that they form one homogeneous phase (Tobolsky, 1960, pp. 81-82). Most of the presently important systems are compatible to the extent that a slight (but usually unknown!) degree of mixing takes place, or interfacial bonding is developed directly, as in grafts or blocks.

The experimental evidence for phase separation in polymer mixtures was briefly developed in the previous section. In the present section a thermodynamic explanation for mutual insolubility, or incompatibility, of polymer pairs will be outlined.

Polymer incompatibility arises from the very small entropy gained by mixing different kinds of long chains. In fact, it will be shown that in the limit of high molecular weight, only polymer pairs with zero or negative heats of mixing form one phase. Let us first develop the history of polymer incompatibility studies, since this offers insight into the status of our understanding and shortcomings at the present time.

Dobry and Boyer-Kawenoki (1947) investigated the phase relationships existing in ternary systems: polymer (1)-polymer (2)-mutual solvent (3). They prepared dilute solutions of polymers in common solvents, and then mixed the two solutions of interest. All of the polymer pairs studied were found to undergo phase separation at only 5-10% polymer concentration. For instance, cellulose acetate and polystyrene were immiscible at 5% concentration in toluene. These investigators concluded that incompatibility of two polymers even highly diluted is the normal situation.

2.5.1. Thermodynamics of Mixing

Shortly thereafter, Scott (1949)* offered a theoretical explanation of the Dobry and Boyer-Kawenoki results; specifically, he investigated the partial molal free energy of mixing $\Delta\bar{F}$ of polymer-polymer binary systems, and polymer (1)-polymer (2)-solvent (3) ternary systems. For binary polymer-polymer systems, $\Delta\bar{F}$ is given by

$$\Delta\bar{F}_1 = RT \left[\ln v_1 + \left(1 - \frac{m_1}{m_2} \right) v_2 + m_1 \chi_{12} v_2^2 \right] \quad (2.8)$$

* Note especially the section, "The Two Polymer System."

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Polymer-Polymer Miscibility

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At present, the appearance of a single glass transition for polymer blends is not universally accepted as evidence of mixing at the macromolecular scale, to say nothing of the segmental scale [15]. Acceptable experimental evidence supporting unambiguously either side of this question is lacking, and the level of mixing required to produce a single T_g is actively being sought. The best studies to date [16] tend to show that the level of mixing in blended systems with a single T_g is essentially the same as that in a pure component, where each macromolecule tends to exclude measurably its neighbors. Thus, it does not appear likely that mixing on a segmental scale occurs, except in the special, but not uncommon, circumstance of strong specific interactions.

Microscopic evidence of two-phase behavior has been found in several cases where bulk properties imply single-phase behavior [17, 18]. However, electron microscopic examination of pure amorphous homopolymers (e.g., atactic polystyrene) has revealed domain structures as well [5]. Small-angle neutron scattering studies, on the other hand, show only random chain conformation in amorphous polymers. The latter technique is currently being applied to polymer-polymer systems and should provide important insight into the structure of single-phase and two-phase polymer systems [19].

Numerous *experimental* studies of phase behavior using bulk, or "macroscopic," properties such as glass transition have demonstrated that many polymer blends exhibit neither true two-phase behavior nor single-phase behavior. From these intermediate cases, two classes of behavior can usually be constructed:

- (1) Two-phase structure where both phases contain different and finite concentrations of each component, as revealed by T_g values shifted significantly from the pure-component values. This behavior is analogous to that found with low molecular weight systems.
- (2) Multiphase, or interphase, behavior where the glass transition is broadened over that commonly observed in single-phase systems.

These intermediate cases, shown schematically in Fig. 1.2, are quite common and will be covered in this treatise (Chapters 3, 5, and 6).

The vast majority of polymer pairs form two-phase blends after mixing as can be surmised from the small entropy of mixing for very large molecules. These blends are generally characterized by opacity, distinct thermal transitions, and poor mechanical properties. However, special precautions in the preparation of two-phase blends can yield composites with *superior* mechanical properties. These materials play a major role in the polymer industry, in several instances commanding a larger market than either of the pure components.

A typical example is impact-modified polystyrene (IPS), shown in Fig. 1.3. In this material, the polybutadiene phase (dark) is bonded to the matrix

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for excluding what is certainly the vast majority of polymer-polymer mixtures. The boundary line will not satisfy all participants—that would take the skills of a master politician—and in many instances some trespassing will occur.

In very general terms, if a blend in question possesses properties analogous to those expected for a single-phase material, the blend will be considered proper subject matter for this treatise. In most instances the critical property will be the glass transition; a blend with a single glass transition will be classified as miscible. Blends of components having similar glass transition temperatures will provide ambiguous cases and other techniques must be employed. But experience has shown that immiscibility in polymer blends is rarely well concealed, revealing itself as opacity, delamination, double glass transition, or combinations of these properties.

From a thermodynamic point of view, every polymer has some solubility in every other polymer, but the magnitude in most cases is exceedingly low. For example, if polystyrene is fluxed on a mill with poly(methyl methacrylate), a *two-phase* mixture results, no matter how long or intensive the mixing. One could, in principle (but with difficulty in practice), separate the two phases, analyze the composition of each, and arrive at values for the mutual solubilities. In this case, as with hexane in water, the solubilities would be less than 1%.

On the other hand, if one fluxes polystyrene on a mill with poly(2,6-dimethyl-1,4-phenylene oxide) as the second component, one phase results. It is thermodynamically stable because no matter how slowly the mixer turns or how long one waits there is still only one phase.

Consider a third example: polystyrene (PS) plus poly(vinyl methyl ether) (PVME). If PS is fluxed with an equal amount of PVME on the mill at 80°C, a clear, one-phase mixture results. However, if the temperature is raised to 140°C, two phases appear. A return to 80°C restores one phase. This behavior has been summarized for a range of compositions by the experimental cloud-point curves shown in Fig. 1.1.

These three examples provide an excellent basis on which to build a definition of polymer miscibility. The first represents an example of an immiscible blend, the second a miscible blend; the third illustrates that miscibility and immiscibility can be exhibited by the same mixture depending on the ambient condition. Furthermore, the third example demonstrates that the driving forces for the transition from the one-phase (miscible) to the two-phase (immiscible) state are thermodynamic in origin and do not depend, for example, on the extent or intensity of mixing.

In spite of the seemingly unquestionable behavior described in these examples, an exact definition of miscibility in polymer mixtures is a subject of considerable debate because it represents different characteristics to dif-